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Benkoski, Jason, J.

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The Johns Hopkins University Applied Physics Laboratory
11100 Johns Hopkins Rd
Laurel, MD 20723

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14. ABSTRACT

The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.

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POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #8

Prepared for:

Clifford W. Anderson
Logistics S&T Thrust Manager
Office of Naval Research
Code 30, Room 1149
875 North Randolph Street
Arlington, VA 22203-1995

Prepared by:

Jason J. Benkoski, Ph.D., Senior Research Scientist
The Johns Hopkins University Applied Physics Laboratory
The Milton S. Eisenhower Research Center
11100 Johns Hopkins Rd, MS 21-N109
Laurel, MD 20723
Tel. (240) 228-5140

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1 Summary

We have now observed self-healing in real time using electrochemical impedance spectroscopy. Although others have demonstrated self-healing through microscopy or mechanical measurements, this is one of the first direct measurements of corrosion prevention through self-healing. Initial salt spray measurements suggest that the corrosion prevention of our self-healing coatings is comparable to zinc-filled primers. Early data suggests microcapsules rich in Octadecyltrimethoxy silane (OTS) outperform polyurethane resin-filled microcapsules, supporting the hypothesis put forth in the FY12 proposal and showing initial proof-of-concept for some of our proposed Polyfibroblast design changes. PPG has successfully scaled up to produce 1-gallon batches of self-healing paint. This was one of the main goals for FY11. Full chemical characterization of the metal shell is complete. It shows that we are achieving the desired levels of zinc and do not see large-scale inhomogeneity in the composition of the alloy.

2 Project Goals and Objectives

PPG has demonstrated the ability to scale up to 1-gallon batches, which was the major milestone of this year. The only milestone remaining is to show that microcapsules can withstand one week at 100°F and 100% relative humidity without losing liquid. Our continuing technical challenges may be overcome by the switch to silane adhesion promoters, which are less prone to moisture-induced polymerization compared to diisocyanates.

3 Key Accomplishments

3.1 Direct Electrochemical Measurement of Self-Healing

Figure 1 is the Bode plot for a sample containing a mixture of uncoated (no metal) microcapsules and zinc powder. The microcapsules contain 25 wt. % MPTMS and they are blended with an equal volume of Zn powder. Together they make up approximately 55 vol% of the cured coating. The samples were tested at room temperature (23 °C) in aqueous ASTM G42 solution, which includes a mixture of 1 wt. % sodium carbonate, 1% sodium sulfate, and 1% sodium chloride. The top two curves represent the impedance taken 6 hours and 0.1 hours before making an incision in the coating. Since the coating had no incision or scratch during the first 6 hours of exposure, the high-frequency impedance does not change with the time of exposure. The decrease in the low-frequency impedance is caused by the infiltration of ions and water into the polymer coating. Therefore, after the incision, the entire curve, particularly the high frequency region, shifts downward to reflect the ingress of the electrolyte. In Figure 1, the bottommost curve represents the impedance taken 0.1 hour after the incision. The curves above that illustrate the recovery of the coating impedance due to the self-healing property of the coating. Full recovery is a slow process, and takes more than 15 hours. The initial loss in impedance due to the scratch and the subsequent healing and recovery becomes more apparent when plotting the magnitude of the impedance at 0.36 Hz versus time in Figure 2.

The other interesting observation was that the scratch healed by foaming (Fig. 3). Under ambient conditions, the resin released by the microcapsules hardens as a thin film within the scratch. The generation of carbon dioxide is too slow to nucleate air bubbles and foam the

polymer. When immersed in water, the polymerization rate is fast enough to foam the polymer as it cures.

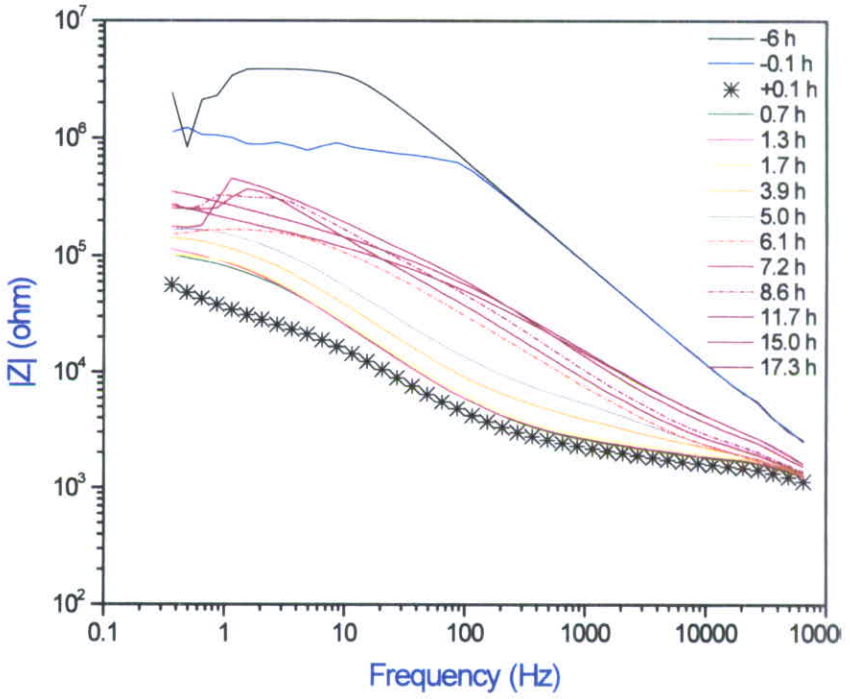

Figure 1: *Bode plot for the sample (25% MPTMS in uncoated microcapsules with 50% Zn powder filler) at room temperature (23 °C) in ASTM G42 solution.*

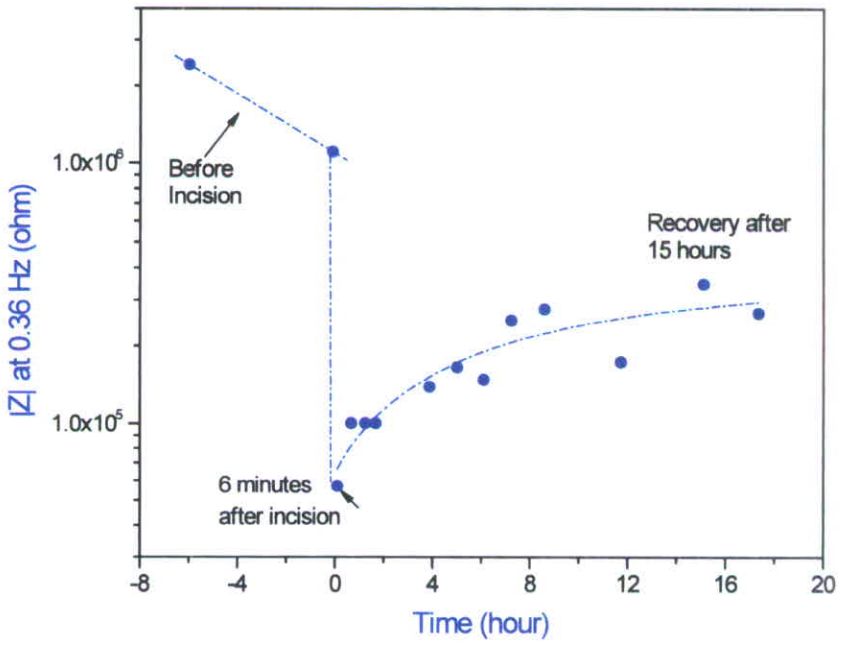

Figure 2: *The magnitude of the complex impedance is plotted versus time. Note how the impedance drops from about 1000 kΩ to 30 kΩ after scratching, but returns to 300 kΩ after 15 hrs. The re-establishment of the impedance is a direct measurement of self-healing.*

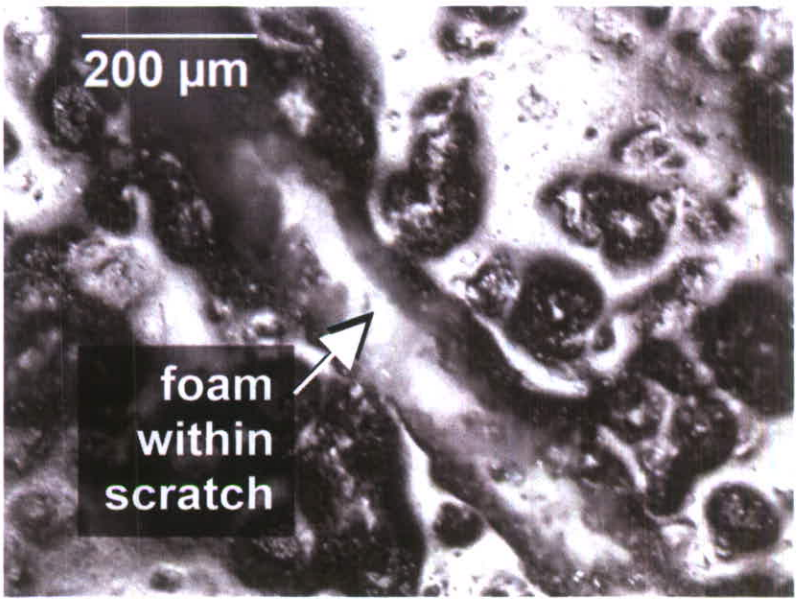

Figure 3: *Optical micrograph of healed scratch corresponding to Figures 1 and 2. In contrast to the thin polymer "scar" that normally form within a scratch, the scratch healed by foaming. The foaming was the result of healing while immersed in water.*

3.2 Salt Spray Measurements

The samples in Table I were evaluated by salt spray measurements for their corrosion protection capabilities. The microcapsules were filled primarily with isophorone diisocyanate (IPDI), and a varying fraction of silane adhesion promoter. The silanes tested included methacryloxypropyltrimethoxy silane (MPTMS), octadecyltrimethoxysilane (OTS), and isocyanatotrimethoxysilane (ITS). Zinc-rich MIL-P-26915 primer served as the control.

Table I: *Sample List for Salt Spray Measurements*

Panels	Percent Silane in Microcapsule Formulation
1B	10% MPTMS
1C	10% MPTMS
2B	20% MPTMS
2C	20% MPTMS
3B	20% OTS
3C	20% OTS
4B	80% OTS
4C	80% OTS
5B	10% ITS
5C	10% ITS
1	MIL-P-Resin w/ZINC

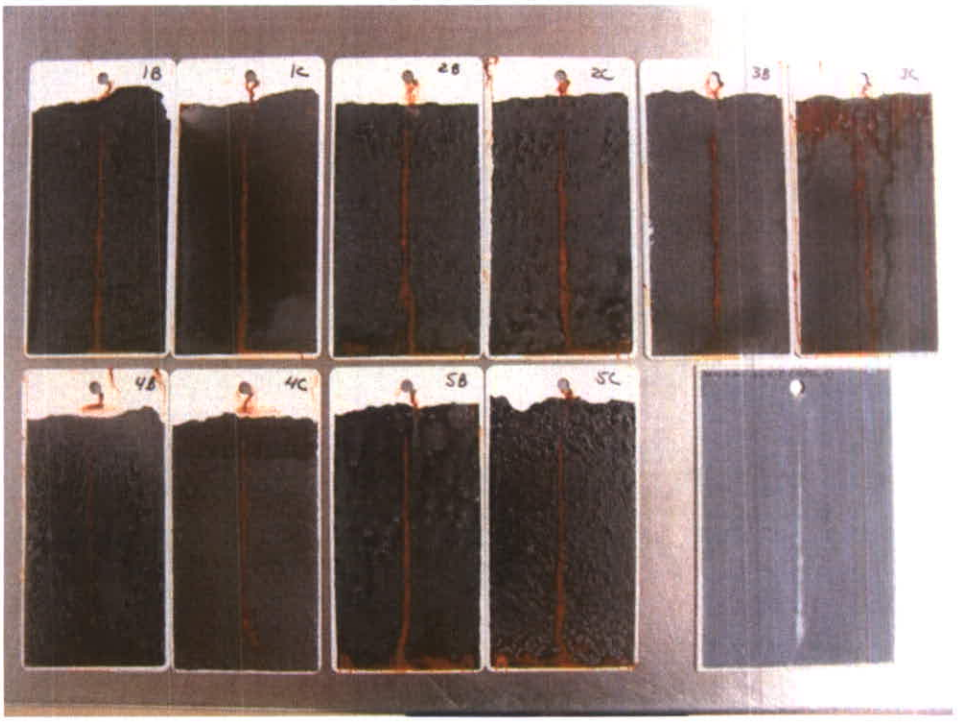

Figure 4: *Salt spray panels after 1 week of exposure. Most panels performed poorly except for 4B and 4C, which were 80% OTS silane. The zinc-rich MIL-P-26915 did not exhibit corrosion in this timeframe.*

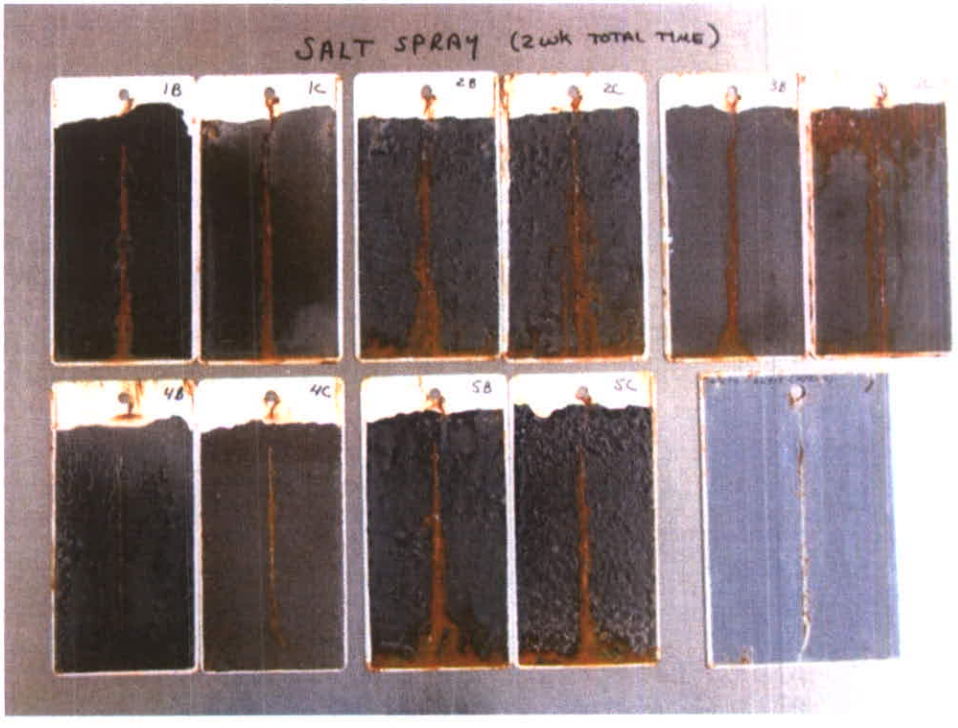

Figure 5: *Salt spray panels after 2 weeks of exposure. Note that the control panel with the zinc-rich MIL-P-26915 primer has begun to rust. The 80% OTS panels (4B and 4C) have shown no increase in rusting since the first week and now show levels of corrosion protection comparable to the MIL-P-26915.*

The most notable feature of the data was how the microcapsules filled with 80% OTS outperformed all other samples. After one week, the MIL-P-26915 control sample still showed less rust than the 80% OTS (Fig. 4), but by two weeks, the galvanic protection began to wear off to the point where the amount of rust on the control sample and the 80% OTS sample were about even (Fig. 5).

The poor performance of the majority of the self-healing coatings was somewhat surprising. Razor blade scratches tend to heal almost regardless of formulation. Also surprising was the fact that the best performing microcapsules contained little or no polyurea precursor. Recall that silanes form a molecular monolayer rather than a thicker polymer film. One explanation for the success of the 80% OTS microcapsules relative to the other formulations is its greater resistance to moisture-assisted polymerization. Despite efforts to improve the hermetic seal of the Ni/Zn shell, the healing capacity frequently decreases over time. Although the other samples in Figure 1 and 2 have been shown to heal in freshly made samples, the coatings tested in these measurements were several weeks old. The only sample that performed to specification was perhaps not surprisingly the sample that possesses the best shelf life.

3.3 Moisture Resistance Testing

Since the Ni/Zn shell has been shown to provide only partial galvanic protection to steel, it has become imperative to begin including Zn powder along with the microcapsules. From a technology standpoint, the Zn increases the size of the sacrificial anode and increases the hardness of the film. From a practical standpoint, the zinc powder is much cheaper than the microcapsules.

Figure 6 summarizes the rust scores for coatings with microcapsules having different silanes (GPS, ITS, MPTMS, and OTS), different fractions of microcapsules versus zinc powder (5-100% microcapsules), and different weight fractions of silane in the microcapsules (1-80% silane). The early trends show OTS performing the best, and performing better at higher weight fractions of silane. The OTS-filled microcapsules also tended to perform better when the filler material was 90-95% zinc powder. Coatings with 25% and 50% microcapsules relative to zinc also performed well, except that the 0.032 in. scratch showed only a small amount of rust. Otherwise, they performed equally well.

Perhaps concerning is the fact that the 0.125 in. scratches did not heal as well as they did with the original Polyfibroblast design. The coatings loaded with 55 vol. % IPDI-filled microcapsules performed best on the 0.003 and 0.125 in. scratches, while having the most difficulty with the intermediate scratch widths. The OTS-filled microcapsules, on the other hand, heal scratches easily up to 0.032 in., but struggle with the 0.125 in. scratches. The difference appears to arise from the effectiveness of releasing IPDI in large volumes. The wider scratches could form a thicker polymer scar because the larger available volume of IPDI. In contrast, the extra OTS does not form a thicker film. It forms a monolayer on the exposed steel, and the excess presumably washes away.

OTS may also perform differently than IPDI due to the underlying design philosophy. For OTS, the goal is to protect primarily by galvanic protection, with the OTS monolayer serving to decrease the galvanic current and therefore extend the lifetime of the sacrificial anode. This method may simply be less effective for wide scratches.

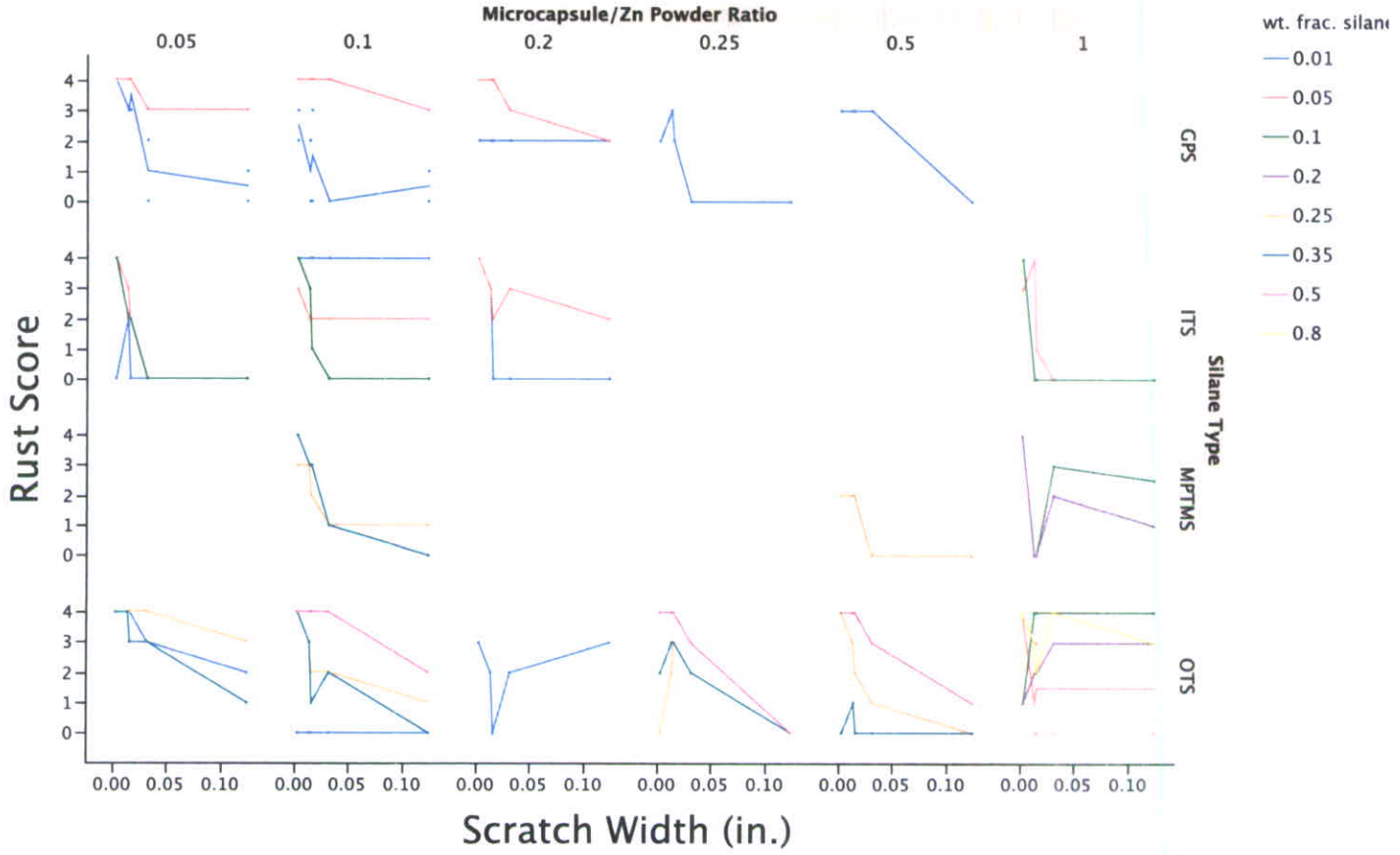

Figure 6: *Compilation of rust score data for the moisture resistance test as a function of scratch width. The data is grouped horizontally according to the fraction of microcapsules relative to the total amount of filler including zinc powder. It is grouped vertically according to the type of silane added to the resin. The fraction of silane in the resin is coded by color according to the legend.*

3.4 Composition Analysis

The composition of the Ni/Zn alloy was measured as a function of the initial feed ratio of the basic Ni/Zn plating bath using three techniques: inductively coupled plasma atomic emission spectrometry (ICP/AES), Auger electron spectroscopy, and Energy Dispersive spectrometry (EDS). Figure 7 presents the three data sets. All three showed essentially the same trend, which was that the alloy composition matched the plating bath feed composition up to about 15% Zn, and then leveled off. Of the three measurements, the ICP/AES is probably the most reliable due to the larger sample size.

Elemental mapping performed by SEM/EDS showed no large-scale inhomogeneity in the composition of the alloy. Ni, Zn, and P appeared to be uniformly distributed throughout the alloy, as shown in Figure 8. The uniform elemental maps do not, however, preclude the possibility of inhomogeneity over smaller length scales. TEM studies performed by other research groups, for example, have indicated some enrichment of Zn at the grain boundaries.

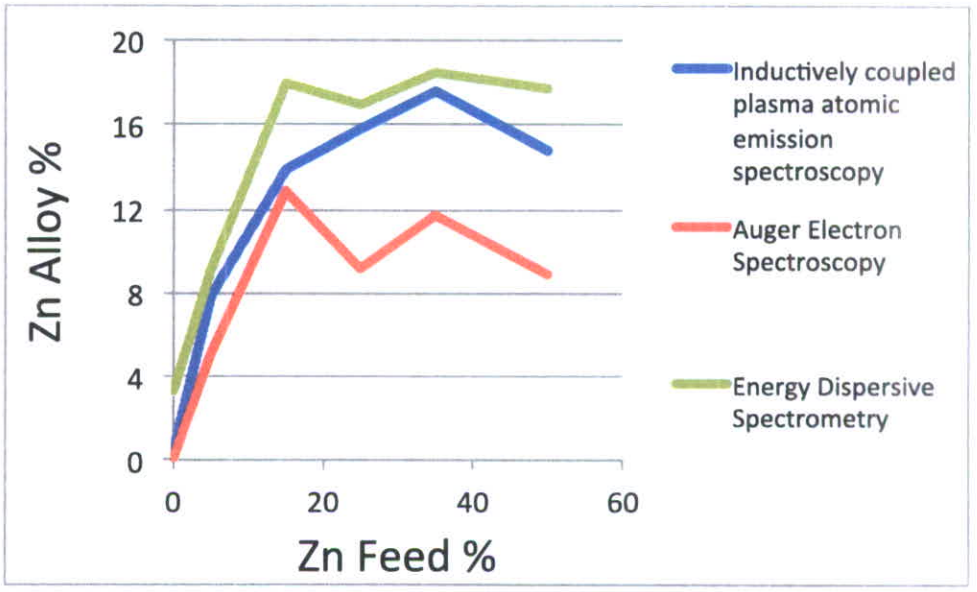

Figure 7: *The mole percent of zinc in the electroless Ni/Zn alloy is plotted versus the mole percent zinc in the plating bath. Results are compared for ICP/AES, Auger, and EDS measurements.*

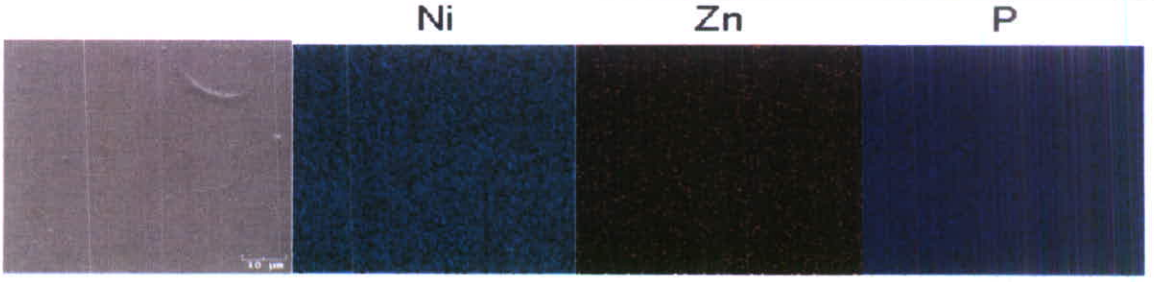

Figure 8: *SEM image of the 15% Zn sample with the accompanying elemental maps for Ni, Zn, and P.*

3.5 Scale Up

PPG identified rotor-stator mixers as the best method for increasing the batch size from 20 g to 1000 g, which is the amount of microcapsules needed for 1 gallon of primer. Rotor-stator mixers not only made for easy translation of JHU/APL's methodologies to PPG's larger batch procedures, but this method, in fact, finds wide use in pilot scale facilities where they are modified for continuous, rather than batch processing. SEM micrographs for this batch of samples are presented in Figure 9 below.

Even as the production of larger batches shows the promise of this technology for industrial scale production, PPG has identified a number of processing steps that need improvement. The largest challenge is still the final drying step. Freeze drying is still the best method for producing dry powders that disperse readily in the primer resin. Unfortunately, this process is slow and consumes large amounts of energy, making it prohibitively expensive.

Another challenge to address is the scalability of the electroless plating process. Prior to plating, the microcapsules are too fragile for vacuum filtration. Slower centrifugation or

sedimentation methods are therefore currently used to purify between processing steps. The adaptation of such tedious purification steps to automated or continuous processes is not entirely straightforward, even as large centrifuges are readily available. This particular challenge does not currently appear to be a deal breaker, but several key technical challenges remain to balance the need to reach high purity with the need to prevent microcapsule rupture.

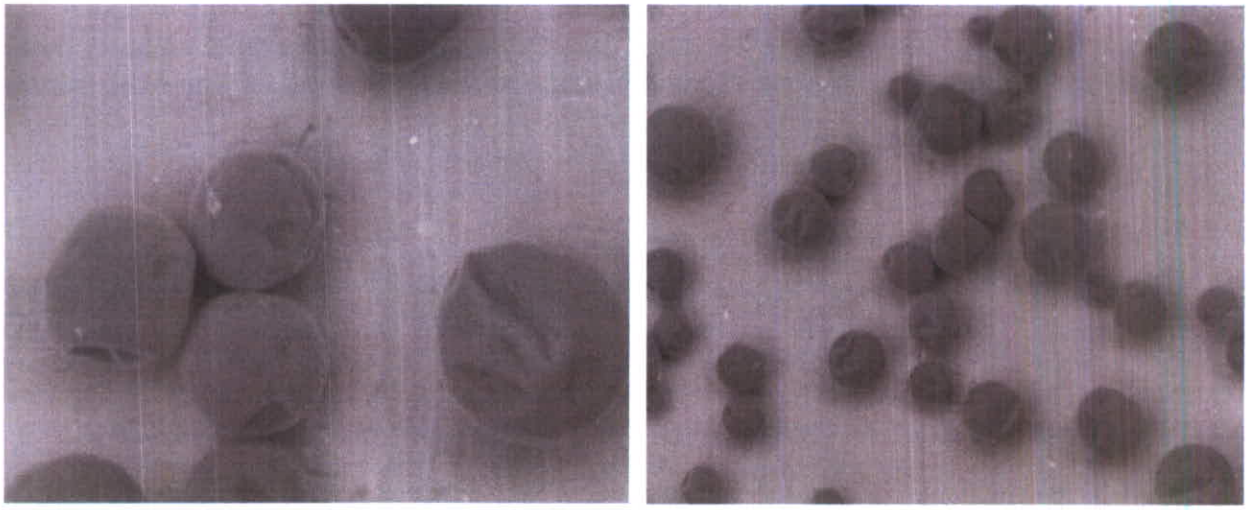

Figure 9: *Ni/Zn-coated microcapsules synthesized in a 1 kg batch. Note the unbroken coating of Ni/Zn and the uniform size distribution. The left image is 123 μm across, and the right image is 300 μm across.*

3.6 Shelf Life

To assess shelf life, PPG performed a test known informally as a hot room experiment, which consists of placing samples at 125°F for one week. This is a standard test to simulate the elevated temperatures encountered by paints during shipping. The results in Table II show that the viscosity of polyurethane resin increased 4-fold with or without microcapsules, but that the doubling of viscosity for the filled epoxy resin was not repeated by the unfilled epoxy resin. Other observations were that the microcapsules only experienced soft settling in the polyurethane resin. The microcapsules in the epoxy resin experienced more of a hard settle, but could easily be redispersed by agitation. Overall, the changes would not preclude use of these primers in a commercial setting.

Table II: *Hot Room results for Polyfibroblast filler in MIL-P-26915 resin (polyurethane resin) and DP90LF resin (epoxy resin).*

		8/4/11		8/11/11
	Fmla wt g	**Viscosity**	**Viscosity**	**Visual**
Polyurethane Resin +	30.00			
Freeze dried particles	7.50			
	37.50	**35 cP**	**125 cP**	**more viscous**

	Fmla wt g	**Viscosity**	**Viscosity**	**Visual**
Epoxy Primer Resin +	30.00			
Freeze dried particles	7.50			
	37.50	**115 cP**	**225 cP**	**more viscous**

	Fmla wt g	**Viscosity**	**Viscosity**	**Visual**
Polyurethane Resin	30.00	**10-15 cP**	**40 cP**	**sl more yellow**

	Fmla wt g	**Viscosity**	**Viscosity**	**Visual**
Epoxy Primer Resin	20.00	**70-65 cP**	**35-45 cP**	**same**

The shelf life results for exposure to high humidity were less encouraging. For these experiments small amounts of microcapsules were placed in a humidity chamber at 100°F. The relative humidity was maintained at a constant level of 92.9% using a saturated potassium phosphate solution. Four samples were tested in all, with different thicknesses of the polymer skin layer. The thickness was varied by changing the amount of time allowed for interfacial polymerization. The thickness is reflected in the initial fraction of liquid, as noted in Table III. Observe that majority of the resin cured in all cases.

Our goal for this year was to achieve a negligible loss in resin when exposed to these conditions. The loss of liquid points clearly to a poor hermetic seal formed by the Ni/Zn shell. This is evidenced by how the uncoated microcapsules fared no worse than the metal coated ones. Even the sample with no metal shell suffered roughly the same loss.

With some samples lasting up to 9 months with retained liquid, it is known that the metal shell can protect the resin when properly synthesized. No evidence of cracks or incomplete coverage in the metal are visible under SEM inspection. The data may therefore imply breaches in the metal shell that are too small to see at these magnifications. Possibly crevices exist at the grain boundaries or other thin portions of the film. Another possibility is that the metal becomes damaged by thermal expansion, rough handling, or corrosion. For future experiments, we plan to synthesize samples with a thicker metal shell by plating for two, three, and four hours. It is clear that the thickness of the polymer skin layer does not affect shelf life.

Table III: *Thermogravimetric analysis of Polyfibroblast microcapsules before and after exposure to 92.9% humidity at 100°F for one week.*

Polymer Skin Thickness	Ni/Zn Shell Thickness	% Liquid Before Humidity Exposure	% Liquid After 1 wk 100°F 92.9% RH	Percent Change
μm	*μm*	*%*	*%*	*%*
2.4	1.3	82%	30%	52%
4.6	1.3	67%	10%	57%
18	1.3	13%	1%	12%
6.9	0	54%	8%	46%

4 Next Steps

4.1 PPG: Primer Characterization

With the large batch of microcapsules now prepared, PPG will use the remaining month to perform as much characterization as possible. They will continue to evaluate shelf life, dispersion, alternate resin formulations, and rheology.

4.2 APL: Silane Optimization and Shelf Life

APL will spend the remaining month acquiring additional data in order to determine the optimum microcapsule formulation for preventing corrosion. APL will also revisit the shelf life issues to see if more careful control of plating conditions can improve the ability to protect the isocyanate monomer.

Award Information

Award Number	N00014-09-1-0383
Title	Polyfibroblast: A Self-Healing & Galvanic Protection Additive
Principal Investigator	Dr. Jason J. Benkoski
Organization	The Johns Hopkins University Applied Physics Laboratory

Technical Section

Objective

Corrosion costs the Department of Defense $23 billion per year, with an estimated $114.5 billion over the next five years. The most effective method to fight corrosion is to apply a protective coating. Unfortunately, the protection is only temporary because of unavoidable wear and weathering. Improvements in durability are handcuffed by the need to spray it from a liquid at room temperature. Rather than pursuing small gains in *damage resistance* under these constraints, JHU/APL has developed *damage tolerant*, self-healing coatings.

Approach

JHU/APL's Polyfibroblast is a paint additive that confers self-healing and galvanic protection to existing military grade primers (Fig. 1). Much like microscopic paint cans, the Polyfibroblast powder consists of microscopic, metallic spheres that are filled with fresh paint. This powder can be added to any off-the-shelf primer. Once the primer is scratched, the microcapsules release their liquid contents into the scratch, where they harden and restore the moisture barrier. If repair is incomplete, the Ni/Zn shell and zinc powder acts as a sacrificial anode to galvanically protect the exposed steel. This design represents a practical approach, where self-healing properties could be gained without the need for paint reformulation, specialized spray equipment, retraining, or significant additional cost.

Progress

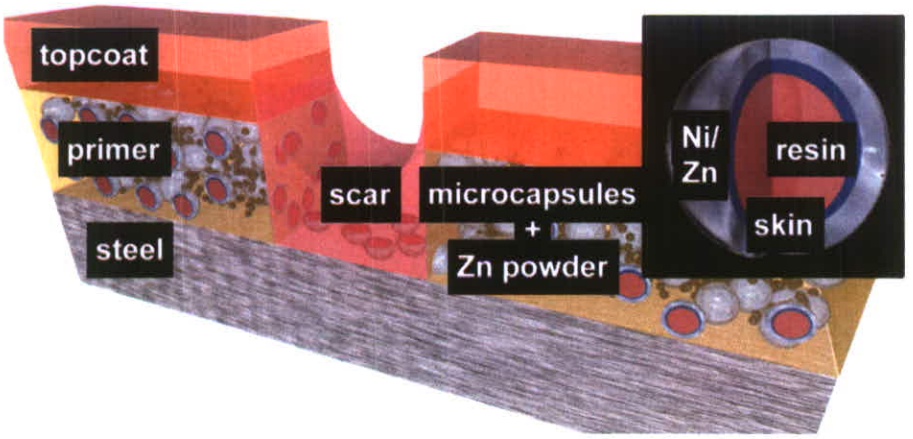

Figure 1. Polyfibroblast contains fresh paint encapsulated in microscopic Ni/Zn shells. When scratched, resin from the broken microcapsules fills the crack to form a polymer scar. Zn powder supplies galvanic protection in the event of incomplete healing.

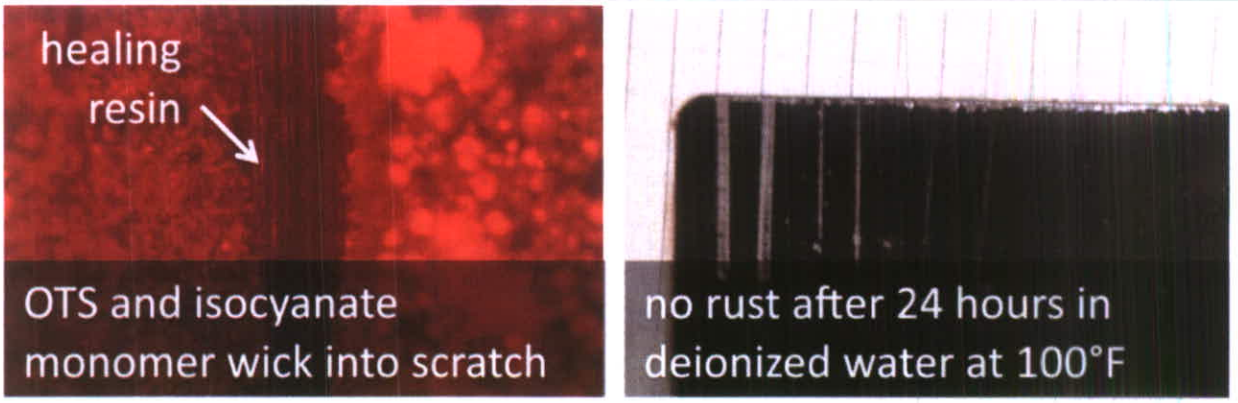

Figure 2: OTS-modified Polyfibroblast panel showing the 1/32 in. scratch under fluorescence microscopy, the red glow within the scratch indicates that OTS promotes spreading across the exposed steel. The scratch healing is completely effective after 24 hours in water.

The original Polyfibroblast design was most successful healing hairline (0.003 in.) and relatively wide scratches (0.125 in.). The former healed due to the small exposed area, while the latter resulted from the correspondingly large volume of liquid liberated by the blunt cutting tool. Intermediate scratches proved most difficult to heal. The healing fluid absorbed into the porous damage zones on either side of the crack rather than spreading across the exposed steel.

In phase II (FY12) the intermediate scratch healing problem was overcome through the use of silane coupling agents (Fig. 2). These molecules are a natural compatibilizer between the polyurea and steel, since the silane head group bonds to steel and the organic tail bonds with the polyurea. Surfactants, in contrast, might actually promote water-assisted crack growth by lowering the energy barrier for water penetration to the polyurea/metal interface.

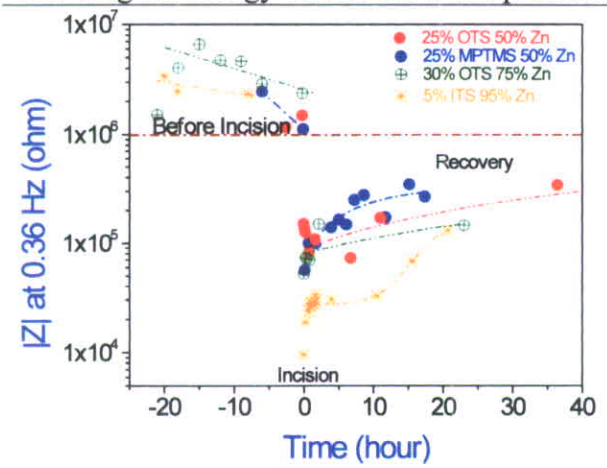

Figure 3. Plot of the magnitude of complex impedance at 0.36 Hz versus time for Polyfibroblast coatings. Impedance spectroscopy directly observes self-healing in real time, and it shows that the extent of healing increases with microcapsule loading.

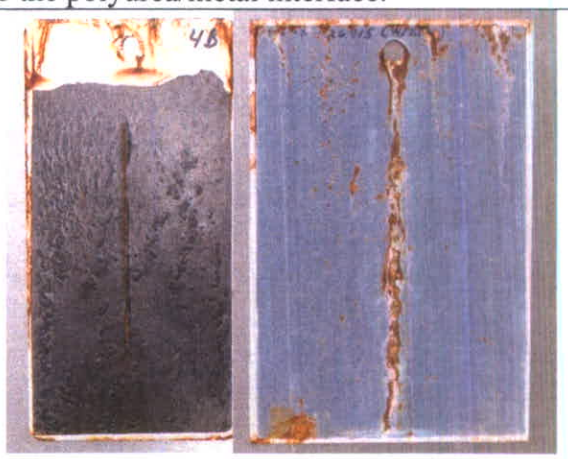

Figure 4. OTS-modified Polyfibroblast panel (left) compared to a MIL-P-26915 zinc rich primer (right) after 4 weeks of salt spray exposure. The self-healing primers outperform the zinc rich primer once the galvanic protection runs out.

Figure 3 represents what may be one of the first direct measurements of corrosion protection by self-healing. The measurements were performed using electrochemical impedance

spectroscopy (EIS) over an area of 14 cm^2. To date, OTS has shown the greatest protection against corrosion. Consisting of 18 methyl units attached to a silanol head group, this molecule spontaneously forms a self-assembled monolayer, with the silanol covalently attached to the substrate and the alkane tails forming a dense brush facing the air. Despite being only 2.2 nm in thickness, this hydrophobic monolayer largely prevents water and salt penetration. After 4 weeks in a salt spray chamber, OTS-filled microcapsules outperformed MIL-P-26915 zinc rich primer, the first time that this has been achieved in our studies (Fig. 4).

Also discovered in FY12 was the fact that the cathodic protection supplied by the Ni/Zn shell was incomplete and perhaps temporary. Electrochemical characterization did not conclusively identify whether zinc depletion was the culprit. Nevertheless, this finding illustrated the risks of using the microcapsules alone. The addition of zinc powder solves this problem by shifting the burden of galvanic protection away from the Ni/Zn shell. This realization has prompted a shift in design paradigm towards using galvanic protection as the first line of defense, and the healing action of silane coupling agents as the supplement.

Cumulative Statistics

Documentation / Publications

M. W. Patchan, L. M. Baird, Y.-R. Rhim, E. D. LaBarre, A. J. Maisano, and J. J. Benkoski "Liquid-Filled Metal Microcapsules," *J. Polym. Sci., Part A: Polym. Chem.*, under review.

C. Challener, "Are Smart Coatings Getting Smarter" *JCT Coatings Tech Magazine*, 2011, 26-32.

Conference presentations/proceedings

Invited Oral Presentation: 2011 Smart Coatings Symposium, February 24, 2011
"Creating Self-Healing Coatings with Galvanic Protection through Paint-Filled Metallic Microcapsules" J. J. Benkoski, M. W. Patchan, E. D. LaBarre, L. M. Baird, A. J. Maisano

Oral Presentation: 2011 American Physical Society March Meeting, March 20, 2011
"Self-Repair of Polymer Films Through Monomer-Filled Ni-Zn Microcapsules," M. W. Patchan, L. M. Baird, Yo-Rhin Rhim, E. D. LaBarre, A. J. Maisano, J. J. Benkoski

Poster Presentation: 2011 Polymers Gordon Research Conference, June 12, 2011
"Self-Repair of Polymer Films Through Monomer-Filled Ni-Zn Microcapsules," L. M. Baird, M. W. Patchan, Yo-Rhin Rhim, E. D. LaBarre, A. J. Maisano, J. J. Benkoski

Invention disclosures/patents

Nonprovisional Patent Application, "Self Healing, Galvanic Protection Additive for Paints and Primers," April 11, 2011.

Students/Postdocs supported by this award

N/A

Other noteworthy recognition

- Received praise and interest from B. L. ("Les") Lee, Program Manager for Mechanics of Multifunctional Materials & Microsystems, AFOSR
- *Paint and Coatings Industry Magazine* will run a feature article on this program in early 2012